Thermotransport of Silver in Liquid Gold*

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Abstract

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A thermotransport study of liquid gold which contained trace amounts of silver has been made. An alloy sample, encapsulated in narrow quartz capillary, was held in a temperature gradient till the stationary state was attained. The sample was analyzed for the solute concentration (c_2) along its length. Silver was observed to migrate to the hot end. The net heat of transport, Q^* , was calculated from the expression

$$d \ln c_2 = \frac{Q^*}{R} d \left(\frac{1}{T} \right)$$

and was found to be

$$Q^*_{Ag} = -1230 \pm 290 \text{ cal/gm-atom}$$

The results are discussed by considering Q^* to consist of two parts, 1) extrinsic part, Q^*_e , which arises from the interaction of electrons with solute ion, and 2) intrinsic part, Q^*_i , arising from the interaction of diffusing ion with its neighboring ions. If Q^*_e is calculated by use of Gerl's method which calculates the energy transfer from electron to solute and Q^*_i is calculated by use of Chapman's expression, fair agreement is obtained between the experimental and calculated values of heats of transport.

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I. Introduction

If a homogeneous single phase alloy is held in a temperature gradient, matter fluxes are usually generated and a concentration gradient will be created by the temperature gradient. This phenomenon is called thermotransport. DeGroot⁽¹⁾ investigated this phenomenon on the basis of the theory of thermodynamics of irreversible processes. This theory characterises thermotransport by a quantity called the heat of transport (Q^*) which, for component i , is defined as

$$Q_i^* = \left(\frac{J_h'}{J_i'} \right) \quad J_j' = 0, \quad \nabla T = 0 \quad (1)$$

i.e., Q_i^* is the flux of heat J_h' transported per unit flux J_i' of species i .

J_h' is the excess heat relative to the average partial molar enthalpy of species i which is carried in the absence of a temperature gradient. The value of the heat of transport is influenced by the details of the dynamics of the diffusion process. Some of these details are not evident in ordinary isothermal diffusion experiments. As a consequence, the results of thermotransport experiments have potential theoretical interest.

The study of thermotransport in liquid metals is in its infancy. There is a great need for a better understanding of diffusion process in liquid metals whereas yet a generally accepted mechanism of diffusion does not exist.^(2,3) Thermotransport studies in liquid alloy systems may help to provide better understanding of the diffusion process. In this respect dilute binary alloys

offer distinct advantages over concentrated alloys. Silver base alloy systems which have been studied by the present authors^(4, 5) appear to be the only dilute binary liquid systems studied so far. In that work the authors reported the results of thermotransport experiments for gold, antimony, sulfur and cobalt in liquid silver. The values of the heat of transport varied widely. None of the existing models of diffusion was able to explain the values of the heat of transport in magnitude or sign. Hence a different model was suggested according to which the heat of transport, Q^* , was considered to consist of two different contributions,

$$Q^* = Q_i^* + Q_e^* \quad (2)$$

where Q_i^* is the intrinsic contribution to the heat of transport. This contribution arises from the interaction between the ions themselves. Q_e^* represents the extrinsic contribution which can arise from a) electrostatic fields created in the metal due to the presence of temperature gradient, and b) interaction of the diffusing ion with the charge carriers which are electrons and/or holes. The extrinsic contribution, Q_e^* , was calculated employing the method due to Gerl.^(6, 7) Q_e^* is significant when the valence of solute differs considerably from that of the solvent. Hence, for an alloy system where both solute and solvent are monovalent, the heat of transport may be expected to be mainly intrinsic. The intrinsic contribution was estimated by use of the expression derived by Chapman⁽⁸⁾ for thermotransport in binary gas mixtures and quite good agreement was obtained between the theoretical and experimental values of the heat of transport for gold in liquid silver.⁽⁴⁾ It appeared proper, therefore, to see whether the thermotransport of silver in liquid gold can be explained in a similar manner.

II. Phenomenological Basis for the Heat of Transport

The term "heat of transport" has not been used consistently either in the theory of thermodynamics of irreversible processes or in relationship to the experimentally observed thermal segregation (the Soret effect) or in discussions of its connection with other atomic properties of liquid metals. Some of these problems associated with the definition of the heat of transport have been described by Tyrell.⁽⁹⁾ The approach to the heat of transport which is used in the present work is described in the Appendix I where an expression has been derived for the heat of transport in relation to the temperature gradient and the concentration gradient at the stationary state. The final expression is (from Appendix I),

$$\frac{1}{R} \left(Q_2^* - Q_1^* \frac{\bar{V}_2}{\bar{V}_1} \right) d \left(\frac{1}{T} \right) = d \ln x_2 = d \ln c_2 \quad (3)$$

where Q_2^* , Q_1^* = heat of transport of solute and solvent respectively

$\bar{V}_2$, $\bar{V}_1$ = partial molar volume of solute and solvent respectively

T = absolute temperature

R = gas constant

x_2 , c_2 = mole fraction, concentration of solute respectively.

In a thermotransport experiment, if a column of liquid alloy is held in a known temperature gradient until the stationary state is reached, the logarithm of the resulting concentration along the length of the column is related to the corresponding reciprocal temperature through the factor $\frac{1}{R} \left(Q_2^* - Q_1^* \frac{\bar{V}_2}{\bar{V}_1} \right)$

which contains the heats of transport of solute and solvent. It may be noted that one obtains only the difference in the heats of transport of solute and solvent, which will be designated as Q^* so that

$$Q^* = Q_2^* - Q_1^* \frac{\bar{V}_2}{\bar{V}_1} \quad (4)$$

III. Experimental

In the technique employed here, a thermotransport experiment consisted essentially in holding a column of liquid alloy of silver and solute in a known temperature gradient for a sufficiently long time for the stationary state to be attained. A description of the experimental part is given here.

A. Thermotransport Apparatus

The apparatus designed for the thermotransport experiments is shown in Fig. 1. It consists of two furnaces placed one above the other and controlled separately. The controller employs platinum-1% rhodium and platinum-13% rhodium thermocouples. These thermocouples are housed in protecting alumina tubes which are closed on one end and placed next to the inside wall of the alumina core on which the heating element is wound. The end temperatures of the sample are measured by use of two Pt-1% Rh and Pt-13% Rh thermocouples, placed adjacent to the sample at the hot end and the cold end respectively.

The temperature along the length of the sample is determined by the following procedure. An alumina tube which is closed on one end is introduced into the furnace assembly through the vacuum fitting on the top. It is lowered down the central cylindrical hole where the sample is normally placed during

the experiment. A reference grade monitoring thermocouple is inserted in this alumina tube. This thermocouple is used to measure the temperature along the axis of the furnace assembly as a function of distance. Thus a temperature profile is obtained which is used to determine the temperature along the length of the sample. In a typical profile the temperature dropped by one hundred degrees in a distance of 6 cms.

B. Experimental Procedure

1. Preparation of Sample

The thermotransport experiments were conducted with gold which contained trace amounts of silver. Gold was obtained from Johnson and Mathey Chemicals Ltd. and was 99.999% pure. The solute element was radioactive silver-110, a gamma emitter. The alloy was prepared by melting together the solute and requisite amounts of gold, and was cast in the form of a rod. Pieces of this rod were used for experiments. The concentration of silver in the alloy was estimated to be of the order of one part per million. The estimation was made from the known specific activity of the isotope. It was not necessary to know the exact value of concentration of solute in the alloy because it is only the relative concentration, not the actual concentration, that is significant in the above concentration range.

The sample consisted of such alloy encapsulated in a narrow, precision bore, quartz capillary with 0.75 mm i.d. Prior to being filled, the capillary was closed on one end and had a long cup attached to the other end. The inside of the capillary was cleaned with several rinses of acetone and methyl alcohol by means of a needle and a syringe and was then dried in an oven. A clean, weighed

piece of alloy was placed in the cup. The amount of alloy was chosen so as to fill the capillary to the desired length which was normally between 5-1/2 and 7 cms. The sample was placed in the filling apparatus which was evacuated and lowered into a tubular furnace. After the alloy was molten in the cup, argon gas was admitted to the system, thus forcing the metal into the capillary. The alloy was allowed to solidify directionally from the bottom upwards. This was accomplished by simply lowering the filled capillary to the cooler parts of the tubular furnace. This procedure prevented any break in the column of the alloy. After solidification, the cup-end of the capillary was attached to a vacuum system. The capillary was sealed under a vacuum of approximately 10^{-4} Torr. Enough room was left in the sealed capillary to accommodate the expansion during melting.

2. Diffusion Annealing

The sealed sample was lowered into the central hole of the dual furnace assembly, until it rested at the bottom. The hole was then closed with a lava plug. A stainless steel cylinder was fitted to the brass vacuum fitting and the furnace chamber was evacuated and power to the furnaces was turned on. The furnaces were controlled in such a way that the metal in the capillary started to melt at the top first and the liquid front moved downwards to the bottom end. The experiments were conducted with 100°C difference between hot and cold ends. The cold end was normally at 1065°C . The variation in the temperature of the hot and cold ends was less than $\pm 2^{\circ}\text{C}$ during a run. The vacuum in the brass chamber was approximately 25 microns of mercury during the anneal.

The approximate time required for achievement of the stationary state (t) is given by⁽¹⁰⁾

$$t = \frac{L^2}{2D} \quad (5)$$

where L = length of the sample

D = diffusion coefficient of solute in silver

A time equal to twice this amount was normally employed in order to ensure that the stationary state was reached. At the end of this period, the sample was allowed to solidify directionally upwards starting from the bottom end. This was accomplished by shutting off the lower furnace first and then the upper furnace a few minutes later, so that a positive gradient was maintained at all times while freezing. The freezing process took 3-4 minutes.

3. Radiotracer Analysis

The metal was separated from the quartz capsule and was thoroughly cleaned with a jet of acetone and methyl alcohol and cut into several sections of approximately equal length. A typical section was 0.5 cm long. Each section was analyzed for the solute activity by use of a scintillation counter which used a 2 π geometry sodium iodide crystal.

C. Some Special Considerations

A few experiments were performed to ensure that any segregation obtained in thermotransport experiments was indeed due to temperature gradient and not due to other factors such as convection, solidification and sedimentation. These special experiments are described below.

The effect of convection is to mix the components and to decrease the amount of segregation. This effect is a strong function of the diameter of

the capillary. Thermotransport experiments were conducted with 0.75 mm and 1.00 mm diameter capillaries. These experiments yielded essentially the same results. This suggested that the observed segregation was not affected by convection.

Verhoeven's⁽¹¹⁾ calculations for such a system predict that the thermal convection (i.e. convection due to the presence of temperature gradient) is quite negligible in this experimental arrangement. The solute convection (i.e. convection caused by the density gradient which results from the gradient in solute concentration), however, may be significant but cannot be calculated accurately for want of data on partial molar volume. Assuming an extreme case where the partial molar volume of solute is five times the molar volume of silver, it is found that solute convection will not set in until the solute gradient exceeds 100 ppm/cm in a one mm capillary, and 300 ppm/cm in a 0.75 mm capillary. Since the concentrations employed here are of the order of a part per million, it can reasonably be assumed that errors due to convection are negligible.

The process of solidification can in principle influence the segregation process. In order to see if this was important, experiments were run for very short annealing time. This was done by introducing the sample into the thermotransport apparatus which was already at the operating temperature. Sufficient time was allowed for the temperature to reach the desired

value. The sample was then removed from the apparatus, sectioned and analyzed. The concentration profile so obtained was very similar to that obtained for the sample that had just been filled. These experiments showed

that segregation due to solidification was not significant in the present experiments, in accordance with Wagner's⁽¹²⁾ calculations which show that segregation due to solidification is negligible for very dilute alloy systems cooled at a rapid rate.

Another factor that can influence segregation is sedimentation. A solute dissolved in a heavier solvent experiences a buoyancy force which tends to concentrate the solute at the top of a vertical capillary. Thus some segregation can occur in an initially homogeneous liquid alloy placed in a gravitational field. In order to see if sedimentation was important in the present investigation, experiments were performed with a negative temperature gradient such that the hot end was at the bottom and the cold end was at the top. A temperature difference of 50°C between hot and cold ends was employed. The results were qualitatively the same as with positive temperature gradient. Calculation of Q^* for the results obtained with negative temperature gradient was not attempted because the amount of segregation which was obtained with 50°C difference was small and consequently the error associated with Q^* was higher.

IV. Results

The concentration of solute in each section is proportional to its specific activity. However, it is not the actual concentration of solute, but the relative concentration that is of interest. The relative concentration (c/c_0) of solute in each section was obtained by dividing its specific activity (c) by the lowest specific activity (c_0) in the sample.

Since the cross-section of the sample was uniform, the length of each section was proportional to its weight. Since the total length as well as the

total weight of the sample was known, the length of each section could be accurately determined. The position of each section was then obtained by simply adding the length of the sections, starting from the bottom-most section. The length of the sample was corrected by the expansion of metal which occurred on melting. This correction was approximately 5-8% and varied with each sample. The amount of shrinkage which occurred on solidification and subsequent cooling was measured from the slightly yellowish mark left by the liquid metal on the inside wall of the capillary.

Since the temperature along the length of the sample was known, the logarithm of relative concentration of each sample can be plotted as a function of the reciprocal temperature. Fig. 2 is a typical plot. It is observed that silver segregates to the hotter regions. The heat of transport can be obtained from the equation

$$\frac{Q^*}{R} d\left(\frac{1}{T}\right) = d \ln c_2 = d \ln c/c_0 \quad (6)$$

or

$$Q^* = R \frac{d \ln (c/c_0)}{d\left(\frac{1}{T}\right)} \quad (7)$$

Since no deviation from linearity can be delineated the plots of $\ln (c/c_0)$ vs $\frac{1}{T}$ are fitted with straight lines by use of at least mean square method. ⁽¹³⁾

The slope of the straight line so obtained yields the value of the heat of transport, Q^* , which are listed in Table I for three different experiments.

The error in the value of Q^* can be obtained by use of the method of least mean squares. ⁽¹³⁾ The standard error so obtained is listed in the Table I

for each sample. The arithmetic mean and the standard deviation of the results as a whole are computed. The value of the arithmetic mean with standard deviation is

$$Q^* = -1230 \pm 290 \text{ cal/gm-atom} \quad (8)$$

An error analysis was made for the experiments⁽¹⁴⁾ and it was found that the principal errors arose from the measurements of temperature and solute activity. Errors due to the finite size of the sections and distortion of temperature profile by the introduction of the sample in the apparatus were negligible. The standard deviation in Q^* would be less with more experiments.

V. Discussion

It was pointed out earlier that thermotransport experiments can, in principle, yield information about the dynamics of the diffusion process. An application of the formalism of irreversible thermodynamics showed the relation between the experimentally observed thermal migration and the heat of transport. The heat of transport, however, is a kinetic quantity and will depend on the precise nature of the mass transport process which is not made evident by the thermodynamic-phenomenological theory. Hence a kinetic theory of mass transport in liquid metals should be able to explain the heat of transport from an atomistic point of view. Several theoretical models of diffusion have been developed primarily to explain the results of isothermal diffusion experiments and have had varying degree of success.^(2, 3) There are other theoretical models developed to describe the force acting on the diffusing species in a temperature gradient.⁽¹⁵⁾ These models are presented and discussed in light of the results obtained in the present

investigation. The new approach to thermotransport which was mentioned earlier in the introduction is discussed in detail.

The heat of transport may be considered to consist of two different contributions, viz. intrinsic contribution and extrinsic contribution. Each contribution is considered separately.

A. Extrinsic Heat of Transport

The contribution to Q_e^* due to electrostatic fields appears to be small for metals in general⁽¹⁵⁾ and is neglected here. The contribution of electrons to the heat of transport in metals can be calculated by use of a method described by Gerl.^(6,7) His procedure is used in this paper, but with a slight modification. Gerl assumes a vacancy mechanism for diffusion which probably is not applicable to liquids. It turns out, however, that the presence of a vacancy has little effect on the force acting on the solute atom subjected to a temperature gradient. Hence, the extrinsic contribution to the heat of transport can be written as

$$Q_e^* = \frac{K_e T}{2} \left(\frac{m^*}{m} \right)^{\frac{1}{2}} (E_F)^{-\frac{1}{2}} A_z (E_F) \left[1 + 2 \left(\frac{dA/A}{dE/E} \right) E_F \right] \quad (9)$$

where K_e = electronic contribution to thermal conductivity

m, m^* = rest mass and effective mass of electron

z = effective charge on the diffusing ion

A_z = resistivity scattering cross-section of solute atom for electrons

E = energy of electrons

E_F = Fermi level

The sign of Q_e^* is determined by the term in brackets in expression (9). If this term is positive, that means that the effective scattering cross-section of hot carriers is more than that of cold carriers in which case the solute tends to segregate to the colder regions. If the effective scattering cross-section of hot carriers is sufficiently smaller than that of cold carriers, Q_e^* is negative and the solute tends to migrate to the hotter regions.

The method of calculating Q_e^* is described in the Appendix II. It is calculated that, for silver in gold,

$$(Q_e^*)_{Ag} = -500 \text{ cal/gm-atom} \quad (10)$$

The fact that Q_e^* is negative for silver indicates that the effective scattering cross-section for resistivity of hot carriers is less than that of cold carriers.

A comparison of the experimental heat of transport (Q^*) with calculated value of extrinsic heat of transport (Q_e^*) for silver in gold indicates that there is little extrinsic contribution to the heat of transport in the case of silver.

This may be accounted for by the fact that both silver and gold are monovalent.

In our earlier paper it was found that Q_e^* for gold in liquid silver is also small. ⁽⁴⁾

It appears, therefore, that the heat of transport in the Ag-Au system is predominately intrinsic.

It may be remarked that the values of Q_e^* as calculated above are only approximate, since they are based on certain assumptions whose validity for liquid metals can be questioned. Since the electronic structure does not change significantly on melting, it would appear that the above method (which has been used for solid metals) can be used for liquid metals to get results which may be essentially correct.

B. Intrinsic Heat of Transport

The values for the intrinsic heat of transport (Q_1^*) can be obtained from the models of diffusion. If, for example, diffusion occurs by a jump mechanism, the Wirtz-Brinkman model^(16, 17) predicts

$$Q_1^* = Q_o - Q_f \quad (11)$$

where Q_o is that part of activation energy for diffusion (Q) received in the original position, Q_f is that part of Q received in the final position of the diffusing atom. However, in liquids, one observes only the difference in the heats of transport of solute and solvent, i.e.,

$$Q_f^* = Q_{2i} - Q_{1i} \frac{\bar{V}_2}{\bar{V}_1} \quad (12)$$

$$= (Q_{2o} - Q_{2f}) - (Q_{1o} - Q_{1f}) \frac{\bar{V}_2}{\bar{V}_1} \quad (13)$$

If the hole theory is applicable to diffusion in liquid metals, $Q_o \approx 0$, $Q_f \approx Q$, the activation energy. This is so because according to the hole theory the energy of hole formation accounts for most of the activation energy in liquids.

Further assuming that $\bar{V}_2 \approx \bar{V}_1$, one obtains

$$Q_1^* = -Q_2 + Q_1 \quad (14)$$

Substitution of experimental activation energies into equation (14) yield values of the wrong sign for gold in silver. Such a comparison cannot be made for silver in gold at the present time for want of necessary data.

The Cohen-Turnbull model⁽¹⁸⁾ assumes that diffusion would occur by redistribution of free volume which is already present in the liquid. If a critical

fluctuation occurs, an atom moves with the gas velocity (proportional to $T^{1/2}$) into the void. This assumption would yield values for $Q_2^* = Q_1^* = 0$ and thus is not consistent with experimental observations. Calculations employing the fluctuation model⁽¹⁹⁾ or cluster model^(20,21) are not straightforward and will be the subject of further work. In many respects the above models are more solid-like than gas-like in character. It is interesting, therefore, to examine predictions of Q^* that result from treating liquid metals as a dense gas.

A considerable amount of theoretical and experimental work has been done in the area of thermotransport in dilute gas mixtures (Chapman and Cowling⁽⁸⁾, Hirschfelder, Curtiss and Bird⁽²²⁾). The ions in a liquid metal may be considered to form a dense gas. Theoretical study of thermotransport in dense gas mixtures has been rather limited and no experimental data seem to exist. Of the various methods used to treat dense fluids, Enskog's method employs the gas-like formalism and has been used to describe thermotransport in dense binary gas mixtures.⁽⁸⁾

In the kinetic theory of dilute gases it is assumed that there are only two body collisions and that the molecular diameter is small compared with the average distance between the molecules. Both these assumptions are valid in dilute gases but in dense gases, however, these assumptions must be reconsidered. Enskog was the first to make an advance in this direction by developing a kinetic theory of dense gases made up of rigid spherical molecules. For this special model there are essentially no three body or higher order collisions. By considering only two body collisions and by taking into account the finite size of the molecules, he was able to graft a theory of dense gases onto the dilute gas theory developed

earlier. He showed that the frequency of collisions in a gas made up of rigid spheres differs by a factor χ from that in a gas made up of point particles. This factor χ is intimately related to the equation of state. ⁽²²⁾

The coefficient of self-diffusion in a dense gas is given by ⁽²³⁾

$$D_{(\text{dense gas})} = \frac{D_{(\text{dilute gas})}}{\chi} \quad (15)$$

Such an approach has been used by Ascarelli and Paskin ⁽²³⁾ to calculate the self-diffusion coefficient of mercury, indium and tin. Their theory employs van der Waals concept of a dense fluid in which the attractive potential energy is thought of as a uniform negative potential. This is justified for liquid metals on the basis of pseudopotential theory according to which the attractive part of the interaction energy between electronically screened ions is comparable to that found in rare-gas liquids. ⁽²⁴⁾

Enskog's method yields rather complicated expressions for thermotransport in dilute and dense gas binary mixtures. However, simpler expressions have been derived by Clark Jones for dilute isotopic mixtures ⁽²⁵⁾ and by Chapman ⁽⁸⁾ for dilute binary mixtures. For isotopic mixtures Clark Jones obtains,

$$\begin{aligned} \frac{Q_1^*}{RT} &= \frac{15(C-1)(1+A)}{A(11-4B+8A)} \left(\frac{m_2 - m_1}{m_2 + m_1} \right) \\ &= K \left(\frac{m_2 - m_1}{m_2 + m_1} \right) \end{aligned} \quad (16)$$

where m_1, m_2 = mass of components 1 and 2 respectively.

A, B, C = integrals evaluated from the law of force between the atoms.

The expression is correct to the first power of $\left(\frac{m_2 - m_1}{m_2 + m_1} \right)$ which is assumed to be small. Chapman extended this to the case of binary mixtures by taking the size effect into account. He obtains the following expression,

$$\frac{Q_1^*}{RT} = \frac{5(C-1)}{11-4B+8A} \left[\frac{3(1+A)}{A} \left(\frac{m_2 - m_1}{m_2 + m_1} \right) + 2 \left(\frac{s_2^2}{s_{21}^2} - 1 \right) x_2 - 2 \left(\frac{s_1^2}{s_{12}^2} - 1 \right) x_1 \right] \quad (17)$$

where s_1, s_2 , are equivalent molecular diameters (equal to molecular diameters for a rigid sphere model) and x_1 and x_2 are the mole fractions of the components 1 and 2 respectively. The term s_{12} is equal to $(s_1 + s_2)/2$. For a very dilute mixture ($x_2 \ll x_1 \approx 1$), the expression assumes the form

$$\frac{Q_1^*}{RT} = \frac{5(C-1)}{11-4B+8A} \left[\frac{3(1+A)}{A} \left(\frac{m_2 - m_1}{m_2 + m_1} \right) - 2 \left(\frac{s_1^2}{s_{12}^2} - 1 \right) \right] \quad (18)$$

The expression is applicable when $\frac{m_1}{m_2}$, $\frac{s_1}{s_{12}}$ and $\frac{s_2}{s_{12}}$ differ only slightly from unity. When the differences in molecular masses and diameters are large, the expression will give only an approximate estimate of the heat of transport. An average value of the factor $\frac{3(1+A)}{A}$ is estimated to be 10.⁽⁸⁾ Hence it is normally the first term involving the mass difference that determines the sign of Q_1^* .

The magnitude of Q_1^* will also depend on the value of the factor K which in turn depends on the value of the integrals A , B and C . These integrals can be evaluated if the interionic potential is known. However, the factor K

can also be evaluated from the results of isotope thermotransport experiments. In fact, the latter method will be more accurate than evaluation of K from an arbitrary potential function.

Isotope thermotransport experiments in liquid lithium, potassium, rubidium, gallium and indium have been performed.⁽²⁶⁻²⁹⁾ The value of the constant K for these metals is calculated using the expression (16) and tabulated in Table II. The values of K for different metals lie in a rather narrow range. As a first approximation we will consider K to be independent of the atomic mass and the valence. Hence, this value of K is used in the equation (18) and Q_1^* is calculated for silver in liquid gold.

In Table III are listed the values of Q_1^* so calculated for silver in liquid gold and also for gold in liquid silver for comparison. Both metals are assumed to be monovalent and the corresponding ionic diameters are used for obtaining s_{12} in equation (18). In view of the several approximations made here, the calculated values of the heats of transport of silver in liquid gold and of gold in liquid silver seem to be in reasonable agreement with the experimental values.

Appendix - I

The approach to the heat of transport which is used in the present work is described below. It is different from Lodding's approach^(20, 21) but is similar to the approach of Tichacek et al.⁽³⁰⁾

Irreversible processes occur in a single phase alloy system which is subjected to a temperature gradient. There are flows of heat and matter down the temperature gradient. The parameter which characterizes the course of irreversible processes in such a system is the local entropy production or the product

$$T \sigma = \psi \quad (\text{A-1})$$

where T is the absolute temperature and σ is the rate of entropy production per unit volume. Here ψ is designated as the dissipation function. ψ can be written as

$$\psi = \vec{J}_q \cdot \vec{X}_q + \sum_k^N \vec{J}_k \cdot \vec{X}_k \quad (\text{A-2})$$

$\vec{J}_q$ is the heat current density, $\vec{J}_k$ is the diffusion current density of component k , N is the number of components in the alloy. $\vec{J}_q$ and $\vec{J}_k$ are called generalized fluxes. $\vec{X}_q$ and $\vec{X}_k$ are called the generalized forces. The expressions for $\vec{X}_q$ and $\vec{X}_k$ are

$$\vec{X}_q = - \frac{1}{T} (\text{grad } T) \quad (\text{A-3})$$

$$\vec{X}_k = - T (\text{grad } \frac{\mu_k}{T}) \quad (\text{A-4})$$

where μ_k is the chemical potential of component k . The dissipation function ψ is thus a sum of the products of generalized fluxes and the conjugate forces.

In the case of complete equilibrium, generalized fluxes and forces vanish and $\psi = 0$ corresponding to zero rate of entropy production. In the case of stationary state, the matter fluxes vanish, but not the flux of heat; the generalized forces have stationary non-zero values which do not change with time. ψ has a steady non-zero value. When the system is not in equilibrium, but is near equilibrium, the deviations from equilibrium, i.e. irreversible processes which occur in the system, can be described to a first approximation by homogeneous linear relations between the "fluxes" and the "forces". These relations are called "phenomenological equations". For the case of a single phase alloy held in a temperature gradient, the phenomenological equations can be written as

$$\vec{J}_k = \sum_i^N L_{ki} \vec{X}_i + L_{kq} \vec{X}_q \quad (A-5)$$

$$\vec{J}_q = \sum_i^N L_{qi} \vec{X}_i + L_{qq} \vec{X}_q \quad (A-6)$$

The quantities L_{ki} , L_{kg} , L_{qi} and L_{qq} are the phenomenological coefficients. These coefficients do not depend on the "fluxes" and "forces" but can be arbitrary functions of the local state variables (temperature, concentrations). The phenomenological coefficients satisfy Onsager's reciprocity relations⁽¹⁾

$$L_{ik} = L_{ki} \quad (i, k = 1, 2, \dots, N) \quad (A-7)$$

$$L_{iq} = L_{qi} \quad (i = 1, 2, \dots, N) \quad (A-8)$$

The expressions for the fluxes are simplified for a binary alloy sample which is in the form of a very narrow capillary, several centimeters long. The fluxes and forces are essentially unidirectional (designated as Z direction). The lateral gradients of temperature and concentration are small and are neglected. Hence the vector notation can be dropped for the fluxes and forces.

It is convenient to choose a new set of fluxes, J'_s , which are linear combinations of the original fluxes, J_s ,

$$J'_k = J_k \quad (A-9)$$

$$J'_q = J_q - \sum_k^2 h_k J_k \quad (A-10)$$

where h_k is the partial molar enthalpy of component k. The conjugate forces for the new fluxes are obtained from equation (A-2) which remains unchanged,

$$\psi = J_q X_q + \sum_k^2 J_k X_k = J'_q X'_q + \sum_k^2 J'_k X'_k \quad (A-11)$$

The expressions obtained for the new forces are

$$X'_q = X_q = -\frac{1}{T} \text{grad } T = -\frac{1}{T} \frac{dT}{dz} \quad (A-12)$$

$$X'_k = X_k + h_k X_q = -(\text{grad } \mu_k)_T = -\left(\frac{d\mu_k}{dz}\right)_T \quad (A-13)$$

The new phenomenological equations can be expressed as

$$J'_k = \sum_{i=1}^2 L'_{ki} X'_i + L'_{kq} X'_q \quad (A-14)$$

$$J'_q = \sum_{i=1}^2 L'_{qi} X'_i + L'_{qq} X'_q \quad (A-15)$$

A set of quantities Q_k^* can be defined as

$$L'_{iq} = \sum_{k=1}^2 L'_{ki} Q_k^* \quad (A-16)$$

If this equation is inserted into equation (A-15) with employment of the reciprocity relations (A-7) and (A-8), one obtains,

$$J'_q = \sum_{i=1}^2 \sum_{k=1}^2 L'_{ik} X'_k Q_i^* + L'_{qq} X'_q \quad (A-17)$$

Upon comparison with equation (A-14) one obtains,

$$J'_q = \sum_{i=1}^2 Q_i^* J'_i + (L'_{qq} - \sum_{i=1}^2 L'_{iq} Q_i^*) X'_q \quad (A-18)$$

An expression for Q_i^* is obtained from equations (A-3) and (A-16),

$$Q_i^* = \left(\frac{J'_q}{J'_i} \right) \quad (A-19)$$

$J'_j = 0, \text{ grad } T = 0$

One recognizes the physical significance of the quantities introduced formally by equation (A-16): Q_i^* is the "heat of transport" of component i , that is, the flux of heat transported across a given plane per mole of the moving species i , in excess of the partial molar enthalpy of that species, in the absence of a temperature gradient.

From equations (A-14) and (A-16), one derives

$$J'_k = \sum_{i=1}^2 L'_{ki} (X'_i + Q_i^* X'_q) \quad (\text{A-20})$$

At the stationary state, all the matter fluxes vanish,

$$J'_k = 0 \quad (\text{A-21})$$

$$J'_1 = L'_{11} (X'_1 + Q_1^* X'_q) + L'_{12} (X'_2 + Q_2^* X'_q) = 0 \quad (\text{A-22})$$

Since the system has a fixed volume,

$$\sum_k^2 \bar{V}_k J'_k = 0 \quad (\text{A-23})$$

where $\bar{V}_k$ = partial molar volume of component k . That means

$$\sum_k \bar{V}_k \sum_i L'_{ki} X'_i = 0 \quad (\text{A-24})$$

for an arbitrary X'_i , which means

$$\sum_k \bar{V}_k L'_{ki} = 0 \quad (A-25)$$

For a binary system, equation (A-25) yields

$$\bar{V}_1 L'_{11} + \bar{V}_2 L'_{21} = 0$$

$$L'_{21} = L'_{12} = - L'_{11} \frac{\bar{V}_1}{\bar{V}_2} \quad (A-26)$$

Substituting Eqn. (A-26) in Eqn. (A-22),

$$X'_1 + Q^*_1 X'_q - \frac{\bar{V}_1}{\bar{V}_2} (X'_2 + Q^*_2 X'_q) = 0 \quad (A-27)$$

Substituting the values of the forces in the above equation one obtains,

$$-\left(\frac{\partial \mu_1}{\partial z}\right)_T - \frac{Q^*_1}{T} \cdot \frac{dT}{dz} - \frac{\bar{V}_1}{\bar{V}_2} \left[-\left(\frac{\partial \mu_2}{\partial z}\right)_T - \frac{Q^*_2}{T} \cdot \frac{dT}{dz} \right] = 0 \quad (A-28)$$

The Gibbs-Duhem equation yields

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \quad (A-29)$$

where x_1, x_2 are the mole fractions of components 1 and 2 respectively. Hence

$$d\mu_1 = - \frac{x_2}{x_1} d\mu_2 \quad (A-30)$$

If $\mu_2 = (\mu_{02})_{T,P} + RT \ln x_2$ for ideally dilute solutions,

$$d\mu_2 = \frac{RT}{x_2} dx_2 \quad (A-31)$$

Substituting the values of $d\mu_1$ and $d\mu_2$ in equation (A-28) one obtains,
for diffusion along Z-direction,

$$-\frac{x_2}{x_1} \frac{RT}{x_2} \frac{dx_2}{dz} + \frac{Q^*_1}{T} \frac{dT}{dz} - \frac{\bar{V}_1}{\bar{V}_2} \left[\frac{RT}{x_2} \frac{dx_2}{dz} + \frac{Q^*_2}{T} \frac{dT}{dz} \right] = 0 \quad (A-32)$$

Rearranging,

$$\left(\frac{1}{\bar{V}_1 x_1} + \frac{1}{\bar{V}_2 x_2} \right) \frac{dx_2}{dz} = - \frac{1}{RT^2} \left(\frac{Q^*_2}{\bar{V}_2} - \frac{Q^*_1}{\bar{V}_1} \right) \frac{dT}{dz} \quad (A-33)$$

In the case of a very dilute alloy, one can make the following approximation

$$x_1 \approx 1, x_2 \ll x_1, \quad \frac{1}{\bar{V}_1 x_1} + \frac{1}{\bar{V}_2 x_2} \approx \frac{1}{\bar{V}_2 x_2}$$

and equation (A-33) becomes,

$$\frac{1}{R} \left(Q^*_2 - Q^*_1 \frac{\bar{V}_2}{\bar{V}_1} \right) d\left(\frac{1}{T}\right) = d \ln x_2 = d \ln c_2 \quad (A-34)$$

where c_2 is the concentration of the solute.

Appendix - II

A. Calculation of Q_e^* for Silver in Liquid Gold

Gerl⁽⁷⁾ derived the following expression for the electronic force acting on a solute ion in solvent matrix,

$$F_z = -M A_z(E_F) (1+2E_F\alpha) \quad (A-35)$$

The various quantities on the right hand side of equation (A-35) are calculated as follows,

$$(a) \quad M = \left(\frac{m^*}{2 E_F} \right)^{\frac{1}{2}} K_e \quad (A-36)$$

where m^* = effective mass of an electron

E_F = Fermi level

K_e = electronic part of thermal conductivity

Assuming $m^* = m$,

$$\begin{aligned} K_e &= 1/2 (K_e)_{\text{solid}} \text{ (from Mott and Jones}^{(31)} \text{)} \\ &= 1.04 \times 10^7 \text{ erg/cm-deg C} \end{aligned}$$

one obtains, $M = 0.077 \text{ erg/cm}^2\text{-deg C}$

(b) A_z , the scattering cross section for electrons is obtained from the relation,

$$A_z = \frac{\sum i}{0.211 E_F^{1/2}} \text{ \AA}^2$$

where $\zeta_i = \frac{\partial \rho}{100 \partial c_i}$, resistivity-concentration coefficient. From the

work of Howe and Enderby⁽³²⁾ one obtains

$$\zeta_i = 0.25 \mu\Omega/\text{atom } \%$$

$$E_F = 5.2 \text{ ev for gold}$$

$$\text{Hence } A_z = 0.52 \text{ \AA}^2$$

(c) α_1 is obtained from the expression

$$\frac{dS}{100 dc_i} = (\alpha_1 - \alpha_c) \frac{0.0243 \zeta_i}{\rho T} \quad (\text{A-37})$$

where S = thermoelectric power of liquid gold-silver alloy

ρ = resistivity of gold

$$\alpha_c = \frac{S_T}{0.0243 T} - \frac{1}{2E_F}$$

where S_T = thermoelectric power of pure liquid gold.

For gold-silver system,

$$\frac{dS}{100 dc_i} = -0.2 \frac{\mu\text{V}}{^\circ\text{C}} \quad (\text{Howe and Enderby}^{(32)})$$

$$\rho T = 22.7 \times 10^{-3} T \mu\Omega\text{-cm}$$

and α_1 is then found to be

$$\alpha_1 = -0.696 (\text{ev})^{-1}$$

Hence, the force F_z is calculated to be

$$F_z = + 0.156 \times 10^{-4} \text{ ev/deg C} \quad (\text{A-38})$$

Hence, the extrinsic contribution to the heat of transport is

$$\begin{aligned} (Q_e^*)_{Ag} &= - F_z T \\ &= -0.0218 \text{ ev at } 1395^\circ\text{K} \\ &= -500 \text{ cal/gm-atom} \end{aligned} \quad (\text{A-39})$$

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Table I

Capillary diameter (mm)	Heat of Transport Q^* (cal/gm-atom)	Standard Error (cal/gm-atom)
0.75	- 1,154	$\pm$ 149
0.80	- 1,628	$\pm$ 126
0.80	- 921	$\pm$ 127

Table II

Reference	Metal	Atomic Weight	$K = \frac{15(C-1)(1+A)}{A(11-4B+8A)}$
(26)	Lithium (6-7)	7	2.03
(27)	Potassium (39-41)	39	1.92
(27)	Rubidium (85-87)	85.5	2.54
(27)	Gallium (69-71)	69.7	2.38
(29)	Indium (113-115)	114.8	2.11

$K \text{ (Average)} = 2.2$

Table III

Solute Element	Intrinsic Heat of Transport Q_i^* (cal/gm-atom)	Extrinsic Heat of Transport Q_e^* (cal/gm-atom)	$Q^* = Q_i^* + Q_e^*$ Calculated (cal/gm-atom)	Q^* Experimental (cal/gm-atom)
Silver in Gold	- 1,860	- 500	- 2,360	- 1,230
Gold in Silver	+ 1,770	- 480	+ 1,290	+ 1,690

List of Figures

Fig. 1 Thermotransport apparatus.

- 1 vacuum fitting
- 2 vacuum connection
- 3 brass vacuum chamber
- 4 thermocouples
- 5 lava plug
- 6 stainless steel supporting plates
- 7 platinum wire
- 8 platinum furnace
- 9 carbon core
- 10 sample
- 11 stainless steel cylinder
- 12 Kanthal furnace

Fig. 2. $\ln c/c_0$ vs the reciprocal of absolute temperature
for silver in gold.